

XB → FLA



10

**PCT**WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau

## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification <sup>7</sup> : <b>C08F 2/32, 290/06, C08G 81/02</b>	<b>A1</b>	(11) International Publication Number: <b>WO 00/35961</b> (43) International Publication Date: <b>22 June 2000 (22.06.00)</b>
<p>(21) International Application Number: <b>PCT/US99/29177</b></p> <p>(22) International Filing Date: <b>9 December 1999 (09.12.99)</b></p> <p>(30) Priority Data: <b>60/112,306</b>      <b>14 December 1998 (14.12.98)</b>      <b>US</b></p> <p>(71) Applicant: <b>RHODIA INC. [US/US]; 259 Prosect Plains Road, CN-7500, Cranbury, NJ 08512-7500 (US).</b></p> <p>(72) Inventors: <b>YEUNG, Dominic, Wai, Kwing; 3661 Golden Orchard Drive, Mississauga, Ontario L4Y 3J2 (CA). LIU, Leo, Zhaoqing; Apt. #705, 3575 Kaneff Crescent, Mississauga, Ontario L5A 3Y5 (CA). LANGLOIS, Bruno, R., C.; 32, avenue Emile Zola, F-91700 Sainte Geneviève des Bois (FR). CHARMOT, Dominique; 10, rue Colette Audry, F-93310 Le Pré Saint Gervais (FR). CORPART, Pascale; 3, allée des Erables, F-95510 Sannois (FR).</b></p> <p>(74) Agents: <b>SHEDDEN, John, A. et al.; Rhodia Inc., 259 Prospect Plains Road, Cranbury, NJ 08512 (US).</b></p>	<p>(81) Designated States: <b>AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).</b></p> <p><b>Published</b> <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i></p>	
<p>(54) Title: <b>POLYMERS WHICH EXHIBIT THERMOTHICKENING PROPERTIES AND PROCESS MAKING SAME</b></p> <p>(57) Abstract</p> <p>A polymer produced by polymerizing via water-in-oil emulsion polymerization one or more water soluble monomers with one or more polyalkoxylated monomers wherein said one or more polyalkoxylated monomers contains at least 25 alkylene oxide units and wherein said product demonstrates thermothickening properties, its method of manufacture and use thereof is disclosed.</p>		

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

POLYMERS WHICH EXHIBIT THERMOTHICKENING PROPERTIES AND  
PROCESS MAKING SAME

Background of the Invention

5

1. Field of the Invention

The present invention relates to polymers which exhibit thermothickening properties and the method for forming same. More specifically, the method comprises utilizing an inverse emulsion (i.e., water-in-oil) so that highly concentrated thermothickening polymer emulsions may be formed. The method can involve either the copolymerization of monomers containing multiple alkylene oxide groups or the grafting of alkylene oxide groups onto the chain of a polymer.

15 

2. Technology Description

Reversible thermothickening polymers are known in the art. These polymers represent materials which, when distributed in a solvent, preferably water, increase in viscosity in response to temperature increases but once a certain temperature is reached, the viscosity of the solution will plateau and perhaps ultimately decrease with increasing temperature. The reversible effect comprises that cooling the thickened polymer will cause a reduction in the viscosity of the polymer solution. The goal in using such polymers in industrial applications is to have them exhibit a desired thickening profile at specified temperatures.

25

These polymers are typically hydrophobically modified water soluble polymers. They are essentially water-soluble (hydrophilic) polymers containing a small portion of hydrophobic groups usually in the form of pendant side chains or terminal end groups. In aqueous media, the hydrophobic groups present in these polymers associate, thus creating the unusual and desired rheological properties. Typically these polymers consist of a water soluble polymer backbone modified with polymer grafts that exhibit a low

30

critical solubility temperature (LCST). When subjected to temperature above this LCST the grafts associate and the resulting viscosity increases due these physical crosslinks.

Examples of references which disclose thermothickening polymers and their potential  
5 uses include the following documents. Hourdet et al., "Reversible Thermothickening of  
Aqueous Polymer Solutions", Polymer, Vol. 35, No. 12, 1994; Sarrazin-Cartalas et al.,  
"Association and Thermal Gelation in Mixtures of Hydrophobically Modified  
Polyelectrolytes and Nonionic Surfactants, Langmuir, Vol. 10, No. 5, 1994; Löyen et  
al., "Reversible Thermal Gelation in Polymer/Surfactant Systems", Langmuir, Vol., 11,  
10 No. 4, 1995; Wang et al., "On the Thermal Gelling of Ethyl(hydroxyethyl)cellulose and  
Sodium Dodecyl Sulfate", Macromolecules, Vol. 30, No.1, 1997; Sigale et al., "Aspects  
of Crosslinking Sulfonated Polyacrylamides from Rheological Studies on Their Gels",  
CCC 0021-8995/97/061067-06, 1996; WO 97/00275; US 4722962, US 5681882 and  
US5478602. To the extent necessary for completion, these documents are expressly  
15 incorporated by reference.

In practice, the prior art has suggested the following method for synthesizing the  
polymers: conventional emulsion polymerization (i.e., oil-in-water emulsion), reverse  
phase polymerization (used in the production of responsive polymer beads), bulk  
20 polymerization, solution polymerization, and micellar polymerization. These  
synthesis methods are limited in that highly concentrated polymer solutions cannot be  
easily produced. Accordingly, it would be desirable to develop a synthesis method  
where high concentrations of thermothickening polymer solids resulting from a  
polymerization technique can be obtained.

25 It is further believed that polymers having a molecular weight of greater than  
2,000,000 daltons (using a size exclusion chromatography method) cannot be  
synthesized using the above-mentioned methods. Accordingly, it would desirable to  
produce polymers having a molecular weight greater than 2,000,000 daltons.

30

Brief Summary of the Invention

In accordance the present invention, an improvement to the process for producing thermothickening polymers which overcomes the problems as discussed above, and provides novel products which can be used for multiple applications is provided. More specifically, the improvement comprises producing the thermothickening polymers by utilizing an inverse emulsion (water-in-oil) synthesis technique.

A first embodiment of the present invention comprises a method for producing a polymer which demonstrates thermothickening properties by polymerizing via water-in-oil emulsion polymerization one or more water soluble monomers with one or more polyalkoxylated monomers wherein said one or more polyalkoxylated monomers contains at least 25 alkylene oxide units; as well as the polymer produced thereby.

A second embodiment of the present invention comprises a method for producing a polymer which demonstrates thermothickening properties by polymerizing via water-in-oil emulsion polymerization one or more water soluble monomers and grafting alkylene oxide groups onto one or more moieties of said polymerized water soluble monomers, wherein said alkylene oxide groups contain at least 25 alkylene oxide units; as well as the polymer produced thereby.

The polymers according to the present invention can be used in any of the following applications: pharmaceutical compositions, oils, lubricants, paints and coatings, liquid cleansers, polishes, food products, waxes, cosmetic and personal care compositions, electrophoresis compositions, chromatography compositions, binding compositions, extrusion compositions, molding compositions, cementing compositions, controlled release compositions, or any other application where the thermothickening nature of the inventive compositions can be utilized.

An object of the present invention is to provide a method for producing thermothickening polymers using an inverse emulsion technique.

Still another object of the present invention is to provide novel thermothickening polymers.

- 5 A further object of the present invention is to provide novel end use compositions which possess thermothickening properties.

These, and other objects, will readily be apparent to those skilled in the art as reference is made to the drawings and the detailed description of the preferred embodiment.

10

#### Brief Description of the Drawings

Fig. 1 represents the salt thickening of the polymer from Example #10 (1%).

- 15 Fig. 2 represents the thermal thickening of the polymer from Example #1 in water or in 15%  $\text{Na}_2\text{CO}_3$ .

Fig. 3 represents the thermal thickening of the polymer from Example #10 in saturated  $\text{Ca}(\text{OH})_2$  or in the presence of 15% (by weight) sodium carbonate.

- 20 Fig. 4 represents the thermal thickening of the polymer from Example #10 (1.0%) in the presence of 15% (by weight)  $\text{Na}_2\text{CO}_3$  ( prepared directly from emulsion or from the precipitated solid)

Fig. 5 represents the shear thickening of a 1% polymer from Example #10 (precipitated solid) in the presence of 20% (by weight) sodium carbonate.

- 25 Fig. 6 represents the thermal thickening of polymers from Examples #3-6 and #1 (0.5% by weight) in the presence of 15% (by weight)  $\text{Na}_2\text{CO}_3$  (prepared from the precipitated solid with  $\text{NaOH}$ ).

Fig. 7 represents the enhancement of thermal thickening of the polymer from Example # 32 in the presence of Rhodasurf LA-7.

Detailed Description of the Preferred Embodiment

In describing the preferred embodiment, certain terminology will be utilized for the sake  
5 of clarity. Such terminology is intended to encompass the recited embodiment, as well  
as all technical equivalents which operate in a similar manner for a similar purpose to  
achieve a similar result.

The present invention relates to the production of thermothickening polymers via the  
10 use of inverse (water-in-oil) emulsion techniques. The polymer is produced by either  
copolymerizing one or more water soluble monomers with a monomer containing at  
least 25 alkylene oxide units or by grafting at least 25 alkylene oxide units onto a  
polymer chain.

15 The first component is one or more water soluble monomers. These materials are  
generically defined as water soluble materials which possess ethylenic unsaturation  
and can be selected from the following classes of monomers:

(1) An ethylenically unsaturated carboxylic acid or acid salts having between about 3  
20 and about 6 carbon atoms. Included in this class of compounds are acrylic acid,  
methacrylic acid, itaconic acid, maleic acid and fumaric acid and their acid salts (i.e.,  
sodium, ammonium or potassium salts) and mixtures thereof.

(2) Acrylamide, alkyl substituted (alkyl represents an alkyl group having between 1 and  
25 about 6 carbon atoms) acrylamides such as methacrylamide, hydroxypropylacrylate,  
N,N-dimethylacrylamide, hydroxypropylmethacrylate, vinyl acetate and vinyl  
pyrrolidone and mixtures thereof.

(3) An ethylenically unsaturated monomer containing one or more sulfonate or  
30 sulfoalkyl groups. Examples of component (c) include the acid (sodium, potassium or  
ammonium) salt of: 2-acrylamido-2-methylpropanesulfonic acid (AMPS), 1-allyloxy-2-  
hydroxy-propylsulfonic acid (AHPS), vinyl sulfonic acid, 2-sulfoethyl methacrylic acid,

or vinyl benzene sulfonic acid and mixtures thereof. Particularly preferred is the sodium or ammonium salt of 2-acrylamido-2-methylpropanesulfonic acid (AMPS).

In particularly preferred embodiments, the water soluble monomers comprise a mixture of acrylic acid and AMPS, with the respective amounts being 0 to about 10 parts of acrylic acid per 100 parts AMPS by weight.

The second component comprises either a monomer which contains at least 25 alkylene oxide units or alkylene oxide units which are grafted onto the side and or end chains of the polymer resulting from the polymerization of the water soluble monomers.

The term alkylene oxide is expressly intended to include ethylene oxide, propylene oxide and butylene oxide units, with mixtures of any of these units as specifically falling within the scope of the present invention. As a general rule, the preferred embodiments will include ethylene oxide and/or propylene oxide units. In addition, as a trend, increasing the number of ethylene oxide units will cause the thermothickening properties to be functional at higher temperatures whereas increasing the number of propylene oxide units will cause the thermothickening properties to be functional at lower temperatures. Accordingly, one skilled in the art should select the appropriate alkylene oxide(s) and in respective amounts to target the polymer to the right thermothickening temperature.

In a first embodiment, the hydrophobic alkylene oxide units are added to the water soluble monomer by selecting and copolymerizing an ethylenically unsaturated monomer containing at least 25 alkylene oxide units. Such monomers include alkoxylated fatty alcohols or ethylenically unsaturated materials (for example, vinyl compounds, acrylate compounds, acrylamide compounds, and the like) containing repeating glycol units. Examples of these materials include tridecyl alcohol having either (a) 50, 100 or 150 moles of ethylene oxide; (b) 75 moles of ethylene oxide and 25 moles of propylene oxide and capped with ethylene oxide; or (c) 45 moles each of ethylene oxide and propylene oxide and capped with ethylene oxide. Commercially



available materials containing the level of alkoxylation desired include the Polyglycol materials sold by Clariant, the Ucon materials sold by Union Carbide, and the Pluronic materials sold by BASF.

- 5 In a second synthesis embodiment, the alkylene oxide units are added to the chain not as being part of an ethylenically unsaturated monomer having alkylene oxide units, but, rather, as directly adding (poly)ethylene oxide and/or (poly)propylene oxide to the water soluble monomers to graft the (poly)alkylene oxide units onto the polymerized water soluble monomer backbone.

10

- The polymerization reaction takes place by utilizing inverse emulsion polymerization. The use of an inverse emulsion system is particularly preferred when it is necessary to produce an emulsion having high amounts of polymer solids. When forming a simple aqueous solution, the multicomponent reactants used to form the polymer tends to produce a solution having very high viscosities with a relatively low amount of polymer solids. Accordingly, for applications where higher levels of solids are needed (i.e., greater than 10 percent) the inverse emulsion polymerization technique should be utilized.

- 20 This technique is well documented; see, for instance CA 1304185 or U.S. 3,284,393. To the extent necessary for completion, these references are expressly incorporated by reference. A stable water-in-oil emulsion is composed of an aqueous phase and an organic phase. The aqueous phase comprises water, the water soluble monomer(s) and either the monomer containing alkylene oxide groups or the alkylene oxides. The pH of the aqueous phase is usually in the range of about 7 to about 9 and is preferably about 8 prior to mixing with the organic phase when using the first, copolymerization method, and about 1 to about 3, and preferably about 2 when the second, grafting method is used.

- 25 The organic phase comprises a hydrocarbon solvent and a water-in-oil emulsifier of low HLB value, preferably below 6. Any known hydrocarbon solvent may be used for this purpose but preferred hydrocarbon solvents are mineral spirits. For reasons of product safety, the mineral spirits should be of low aromatic content or free of aromatic content.

Suitable solvents include those aliphatic hydrocarbon solvents commercially available under the trademarks Isopar K and Isopar M from Esso and Shell Sol 715 and Shell Sol 150 or 160, from Shell. To reduce the volatile organic contents (VOC) associated with the use of organic solvents, solvents which have a high flash point/boiling point may be selected. Such solvents are sold by Witco under the trade designations PD-23 or PD-45. These materials are sold as "white mineral oils". Other oils include naturally occurring vegetable oils and oils sold by Pennzoil under the Drakeol trade name. Processing techniques such as solvent stripping and replacement may alternatively be used to reduce the VOC.

When producing the polymer by utilizing the water-in-oil polymerization technique, the amount of solvent that the aqueous phase is added to typically comprises between about 10 to 90 percent by weight of the entire composition, and more preferably between about 15 and about 25 percent by weight of the entire composition.

Suitable water-in-oil emulsifiers include those which have a HLB of less than 6. Examples include sorbitan esters of fatty acids and a preferred one is sorbitan monooleate, which has a HLB of 4.3. This emulsifier can be used alone or blended with one or more C12 to C15 alcohols ethoxylated with, on the average, three to four ethylene oxide molecules. Other suitable emulsifiers are available from Witco under the trademark Witcomide 511. It is believed that this compound contains approximately 50% unesterified N,N-diethanol fatty amide, the fatty groups present on the emulsifier chain containing approximately 64% oleyl, 33% linoleic and 3% palmityl groups. Approximately 40% by weight of the surfactant is believed to be the monoesterified variation of the compound, the ester group containing 15 to 22 carbon atoms. Additionally, small amounts of diesterified material are also present. Also considered within the scope of the present invention are the Hypermer surfactants sold by ICI.

The polymerization initiator may take the form of many known initiators such as azo, peroxide, persulfate, perester and redox initiators. The amount of initiator added to the solution typically ranges from between about 0.05 to about 2 weight percent of the emulsion with amounts ranging from about 0.1 to about 0.5 weight percent being

particularly preferred. Free radical initiators which may be selected include peroxide materials such as benzoyl peroxide, cumene hydroperoxide, hydrogen peroxide, acetyl peroxide, lauroyl peroxide and persulfates, peresters such as t-butylperoxypivalate,  $\alpha$ -cumylperoxypivalate and t-butylperoctoate, and azo (azobisnitrile) type initiators (water or oil soluble) such as 2,2'-azobis-(2-methylpropanenitrile), 2,2'-azobis-(2,4-dimethylpentanenitrile), 2,2'-azobis-(2-methylbutanenitrile), 1,1'-azobis-(cyclohexanecarbonitrile), 2,2'-azobis-(2,4-  
5 preferred is the use of perester and azo initiators, with  $\alpha$ -cumylperoxypivalate and 2,2'-azobis-(2-methylpropanenitrile) being particularly preferred. The initiators may be added in an inert solvent such as mineral  
10 spirits, water or acetone.

To produce the novel polymer using inverse emulsion polymerization techniques a first aqueous phase is produced by adding the components from which the hydrophobically modified water soluble polymer is to be formed to water. The pH of this phase is  
15 typically between about 7 and about 9. If a chain transfer agent such as isopropyl alcohol is desired, it is typically added to this aqueous phase. The aqueous phase is added to an organic phase which includes the organic solvent and the low HLB surface active agent(s). The resulting mixture is then typically homogenized by the application of shear forces such that the particle size of the monomer emulsion is less than 500  
20 microns. The polymerization initiator is added to the system by using one or more sequential additions. Polymerization takes place at ambient pressures and at a temperature between about 25 and about 45°C under nitrogen purging. The reaction continues such that up to 99.9% of the monomers can be converted to a polymeric form.

25 For some applications, it may be ultimately desirable to invert the produced water-in-oil emulsion so that the aqueous phase is the continuous phase whereas the organic phase is the dispersed phase. Inversion of the water-in-oil emulsion may be accomplished by adding a surface active agent having a high HLB value. In practice, addition of a  
30 surfactant having a HLB of greater than or equal to 9 to a water-in-oil emulsion should adding a surface active agent having a high HLB value. In practice, addition of a surfactant having a HLB of greater than or equal to 9 to a water-in-oil emulsion should

successfully effectuate inversion. Examples of surfactants which can effectively invert the emulsion include the following: nonylphenol ethoxylates (8-15 moles EO) and octylphenol ethoxylates (8-15 moles EO). Preferred is the use of nonylphenol ethoxylates having 9 moles of ethylene oxide.

5

The resulting polymer of the present invention has a molecular weight of greater than about 2,000,000 daltons. The achievement of such a high molecular weight is not believed to be obtainable by conventional polymerization methods, but only through use of the inventive method.

10

For still additional embodiments, once the polymer has been formed and either isolated from its medium or in an inverted (i.e., aqueous polymer emulsion) state, the thermothickening properties of the resulting polymer can be enhanced by the addition of one or more nonionic surfactants in relatively minor amounts, for example, between about 0.1 to about 10 parts per 100 parts by weight of polymer. Particularly preferred nonionic surfactants include fatty acid alcohol ethoxylates such as the chemical sold by Rhodia Inc. as Rhodasurf LA-3, LA-7 and LA-9 (lauryl alcohol ethoxylate (3, 7 or 9 moles ethylene oxide)) sorbiten monooleate, and Hypmer B246 available from ICI. Other potential groups of nonionic surfactants include, but are not limited to the following: aliphatic acid alkoxylates, higher aromatic alcohol alkoxylates, fatty acid amides of alkanolamines, fatty acid amide alkoxylates, propylene glycol alkoxylates, block or random copolymers of ethylene and propylene oxide, higher alcohol polyethylene polypropylene block or random adducts and mixtures thereof. A preferred amount of surfactant is from about 0.25 to about 1.5 weight percent based on the weight of the polymer. The thermothickening enhancement effect is also observed in the presence of high calcium ion concentration.

25

The resulting polymers, optionally containing property modifying surfactants, can be used in the following applications: pharmaceutical compositions, oils, lubricants, paints and coatings, liquid cleansers, polishes, food products, waxes, cosmetic and personal care compositions, electrophoresis compositions, chromatography compositions, binding compositions, extrusion compositions, molding compositions,

30

cementing compositions, controlled release compositions, or any other application where the thermothickening nature of the inventive compositions can be utilized.

The invention is described in greater detail by the following non-limiting examples.

5

### EXAMPLE 1

Into a first vessel, an aqueous phase is prepared containing 243.7 parts of distilled water (a), 160.0 parts of 2-acrylamido-2-methylpropanesulfonic acid (b) (AMPS from  
10 Lubrizol), 40.0 parts of acrylic acid (c), 66.7 parts of Polyglycol B11/700 (d) (from Hoechst) and 12.0 parts of 50% NaOH (e). This phase is formed by dissolving AMPS and acrylic acid in water, mixing in NaOH solution and then adding Polyglycol B11/700.

15 Into a second vessel, an oil phase is prepared by mixing 12.0 parts of sorbitan monooleate (f), 10.0 parts of C12-C15 alcohols ethoxylated with 3 moles of ethylene oxide (g) and 6.0 parts of Hypermer B246 (h) (commercially available from ICI) in 170.0 parts of mineral spirits Shell Sol 151 (i) (commercially available from Shell). The aqueous phase is poured slowly into the oil phase while mixing, and the resulting  
20 mixture is homogenized in a blender for 15-25 seconds. The obtained monomer emulsion is then transferred to a reaction vessel equipped with an agitator, a thermometer, a nitrogen inlet line, a feeding inlet line if required. The emulsion is purged with nitrogen for 1 hour before the reaction starts and maintained throughout the reaction. This monomer emulsion is then polymerized under constant agitation by  
25 using one of the following initiation methods:

Method 1. After purging with nitrogen for 1 hour, 0.010 part of ammonium persulfate in 1.0 part of water is added to the vessel and the contents are heated slowly to 35 °C and held at this temperature for 4 hours. Exothermic reaction is developed after about  
30 10 minutes and will last about 1 hour. Slightly water cooling is applied at the earlier stage of the reaction. After 2 hours reaction, 0.025 part of ammonium persulfate in 3 parts of water is fed into the reaction over 30 minutes. The emulsion becomes more

translucent after 4 hours reaction. At this stage, the temperature is increased to 40-43 °C and the mixture is maintained at this temperature for another 2 hours, during which 0.120 part of ammonium iron (II) sulfate hexahydrate in 2 parts of water is fed to the reaction vessel over half an hour after 1 hour at 40-43 °C, followed by 0.025 part of ammonium persulfate in 2 parts of water over half an hour.

Method 2. The emulsion is heated to 40 °C for an automatic reaction after purging with nitrogen for 1 hour. Exothermic reaction is developed within half an hour at 40 °C. After 2.5 hours reaction, 0.025 parts of ammonium persulfate in 3 parts of water is fed into the reaction vessel over 45 minutes and then 0.120 parts of ammonium iron (II) persulfate in 3 parts of water is fed in the vessel over 40 minutes, followed by 0.025 parts of ammonium persulfate in 3 parts of water over half an hour. After all the initiator is added, the contents are held at 40 °C for another half hour and then cooled to room temperature.

Method 3. After the monomer emulsion is purged with nitrogen for 1 hour, 0.10 part of ammonium persulfate in 1 part of water is added to the vessel and then heated to 35 °C and maintain at this temperature for 4 hours, and then at 41 °C for another hour after addition of 0.050 part of ammonium persulfate in 1 part of water. At this stage, 0.120 part of ammonium iron (II) sulfate hexahydrate in 1 parts of water is added to the reaction, followed by 0.025 part of ammonium persulfate in 1 part of water. The reaction contents are held at 41 °C for another half an hour then stopped. Alternatively, the reaction temperature is also controlled at 45, 50 and 55 °C.

Method 4. After 1 hour of nitrogen purging, 0.020 part of ammonium persulfate in 1 part of water is added to the emulsion and the contents of the vessel are maintained at 25 °C and the cooling is in place. One tenth of 0.120 parts of ammonium iron (II) sulfate hexahydrate in 5 parts of water is fed to the reaction vessel to start the reaction. Exothermic reaction occurs after about 5 minutes and the reaction temperature is controlled at 25-33 °C by water cooling. The rest of the ammonium iron (II) sulfate hexahydrate solution is fed to the reaction in such a way that the temperature can be kept below 33 °C by cooling. After half an hour when the exotherm is becoming

smaller, 0.025 part of ammonium persulfate in 1 part of water is added into the vessel. The feeding rate of ammonium iron (II) sulfate hexahydrate is adjusted so the solution is all added to the reaction vessel in about one hour. The reaction vessel is warmed to 40 °C for an additional hour. Alternatively, ammonium iron (II) sulfate hexahydrate is replaced with ascorbic acid (0.058 part).

Method 5. The contents in the vessel are heated to 37 °C after purging with nitrogen for 1 hour and maintained at this temperature throughout the reaction. 0.20 parts of Trigonox 99-C75 (75% cumyl peroxyneodecanoate) is added to the reaction mixture three times for every 1.5 hour. The reaction is carried out at 37 °C for 5 hours then stopped.

#### EXAMPLES 2-6

In Example #2, Lubricant 50-HB-5100 from Union Carbide is replaced with Polyglycol B11/700, while in Example #3-6, Lubricant 50-HB-3520 partially replaces Polyglycol B11/700. The actual amounts of Polyglycol in Examples #3-6 are listed in Table 1 with the amounts being in parts by weight. The other components in these examples are those in Example #1. Polymerization method 2 is applied for the synthesis of the polymer emulsions.

#### EXAMPLES 7-34

Emulsions are prepared in the same manner as Example #1 with various compositions of (a) to (b) components. These monomer emulsions are then polymerized by using the method(s) specified. These examples are listed in Table 2, with the amounts being in parts by weight and polymerization method(s) in the last column.

#### EXAMPLES 35-39

Into a reaction vessel, equipped with an agitator, a condenser, a gas inlet, are added 150.0 parts of tridecyl alcohol randomly ethoxylated with 50 mol of ethylene oxide

and 50 mol of propylene oxide, 0.070 parts of p-methoxyphenol and 4.54 parts of methacrylic anhydride. The contents are heated at 75-80 °C for 4 hours while purged with air. After the reaction mixture is cooled to 60 °C, 154.0 parts of distilled water is added and reaction is stopped. Other type of poly(ethylene oxide) or its co-polymer with propylene oxide is also methacrylated with this method including Polyglycol B11/700, tridecyl alcohol ethoxylated with 75 ethylene oxide and 25 propylene oxide.

The monomer emulsion is prepared as described in Example #1 by using the polyglycol (d) prepared above while the amount of other components are listed in Table 2. The pH of the aqueous phase is adjusted to 7-8 with sodium hydroxide. The polymerization is carried out by using Method 5 for 5 hours at 37-40 °C. Triganox 99 C-75 is added for every hour of reaction. Polymer sample is isolated by adding the emulsion to excess of acetone.

#### EXAMPLES 40-45

Into a reaction vessel is added 556.0 parts of butyl alcohol randomly ethoxylated with 50 mols of ethylene oxide and 50 propylene oxide (ethylene oxide capped) and 23.1 parts of 25% sodium methylate in methanol. The contents are then heated at 95-100 °C under vacuum for 3 hours and then cooled to room temperature. The reaction vessel is then equipped with an agitator. To the above mixture, 17.8 parts of vinylbenzylchloride (inhibited with 1000 ppm phenothiazine) is added while stirring. The contents are then sealed under agitation overnight. The product so obtained is then mixed with 0.2 parts of p-methoxyphenol, saturated with air and stored at room temperature.

The monomer emulsion is prepared as described in Example #1 by using the polyglycol (d) prepared above, Hypermer B261 (h) rather than B246 is used to prepare the oil phase, while the amount of other components are listed in Table 2. The pH of the aqueous phase is adjusted to 7-8 with sodium hydroxide. Method 2 is used for polymerization. The reaction is carried out at 41 °C for 2 hours after 0.50 parts of Triganox 99 C-75 is added and then at 55 °C for 1 hour with additional 0.30



parts of Triganox 99 C-75. Polymer sample is isolated by adding the emulsion to excess of acetone or ethanol.

#### EXAMPLE 46

5

This example describes the isolation of the polymer from the emulsion of Examples #1-34.

Isolation by  $\text{Na}_2\text{CO}_3$ . 400 parts of emulsion from Example #22 are diluted with 100 parts of mineral spirits. To this stirring emulsion is added is 100 parts of sodium carbonate to yield a slurry (sometimes micro-beads). The mineral spirits are then squeezed out through a 75 micron nylon filter bag. The non-tacky semi-solid is dried in vacuum at 60-100 °C overnight to yield 430 parts of solid product. Alternatively,  $\text{Na}_2\text{CO}_3$  is replaced with 50% NaOH to neutralize and to precipitate the polymer. The isolation is also done without further dilution with mineral spirits. The amount of  $\text{Na}_2\text{CO}_3$  is used, at least, to neutralize the emulsion stoichiometrically or up to 50% in excess.

#### EXAMPLE 47

20 This example describe the characterization of thermothickening properties of the polymers thus made.

The thickening properties of the polymer are characterized by measuring the viscosity against salt concentration (salt thickening), temperature ( thermal thickening) or shear rate (shear thickening). Polymer solution is either prepared with the above isolated solid product or with the inverted emulsion by nonyl phenol ethoxylated with 9 mols of ethylene oxide. The inversion of the emulsion is done by mixing 10.0 parts of the emulsion with 0.50 parts of nonyl phenol ethoxylated with 9 mol of ethylene oxide. The mixture is then diluted with 40.0 parts of water and neutralized with 1.14 parts of 50% (by weight) sodium hydroxide. This solution is then used for thickening characterization.

Sodium carbonate is used as the salt to show salt thickening. An 1.0% polymer solution is prepared either by diluting inverted emulsion or by dissolving the isolated solid in water. The viscosity is recorded either by its own or after each addition of the specific amount of sodium carbonate. The salt thickening profiles are shown in Figure 1.

The thermothickening of the polymer solution is measured by recording the viscosity profile versus the temperature. A 2.0% polymer in water or in saturated  $\text{Ca}(\text{OH})_2$  solution is prepared by dissolving 2 parts of polymer in 98 parts of saturated  $\text{Ca}(\text{OH})_2$  and the viscosity versus temperature is recorded on a Fann 50 rheometer at a shear rate of  $170 \text{ s}^{-1}$  (Figures 2-3). Alternatively, 0.5-1% polymer in 15%  $\text{Na}_2\text{CO}_3$  solution is prepared by dissolving or diluting 0.5-1.0 parts (active polymer) in 85 parts of distilled water and then 15 parts of  $\text{Na}_2\text{CO}_3$  is dissolved in the solution. The viscosity profiles versus temperature (Figures 2-4, 6) are recorded on a Brookfield LV viscometer at 30 rpm ( $36.7 \text{ s}^{-1}$ ).

Shear thickening is measured on a Brookfield Programmable Rheometer with spindle CP51. The polymer solution (1% from precipitated solid) containing 20% (by weight) sodium carbonate is prepared, the viscosity against shear rate is recorded (Figure 6).

#### EXAMPLE 48

This example demonstrates that the non-ionic surfactants enhance the thermothickening of the polymer synthesized in Examples #1-45.

Polymer solution (0.5-1% by weight) is prepared by dissolving the isolated polymer in distilled water. To this solution is mixed in nonionic surfactant (0-2% by weight of Rhodasurf LA-7). If required,  $\text{Ca}(\text{OH})_2$  is added to saturate the solution. The solution is heated and its viscosity at different temperature is recorded on a Brookfield LV viscometer at 60 rpm (shear rate  $76.3 \text{ s}^{-1}$ ). Polymers from Examples #1, #21, #32 (polymerized at 45, 55 °C), #34 (polymerized at 40 °C), #39 and #43 are tested with one or more of the nonionic surfactants, which are C12-15 alcohols ethoxylated with

3, 7 or 9 mols of ethylene oxide (an example of a representative surfactant having 7 mols of ethylene oxide is shown in Figure 7).

**Table 1**

5

Example	Lubricant 50-HB-3520 (MW 3520)	Polyglycol B11/700 (MW 5000)
3	20.0	40.0
4	30.0	30.0
5	40.0	20.0
6	60.0	-

Table 2

Example #	Amount of Components (Parts by Weight)										Polymerization	
	a	b	c	d	e	f	g	h	i	j	Method #	
7	233.3	160.0	40.0	66.7	-	12.8	12.5	6.0	214.3	4.5	4 and 5	
8	249.9	171.4	42.9	71.5	-	10.9	10.7	5.1	183.6	3.9	4, (NH <sub>4</sub> ) <sub>2</sub> Fe(SO <sub>4</sub> ) <sub>2</sub>	
9	249.9	171.4	42.9	71.8	-	10.9	10.7	5.1	183.6	-	4, (NH <sub>4</sub> ) <sub>2</sub> Fe(SO <sub>4</sub> ) <sub>2</sub>	
10	245.0	160.0	40.0	66.7	5.0	12.0	10.0	6.0	170.0	-	4, (NH <sub>4</sub> ) <sub>2</sub> Fe(SO <sub>4</sub> ) <sub>2</sub>	
11	296.0	120.0	30.0	50.0	4.0	12.0	10.0	6.0	170.0	-	4, (NH <sub>4</sub> ) <sub>2</sub> Fe(SO <sub>4</sub> ) <sub>2</sub>	
12	225.0	160.0	40.0	66.7	20.0	12.0	10.0	6.0	170.0	-	4, (NH <sub>4</sub> ) <sub>2</sub> Fe(SO <sub>4</sub> ) <sub>2</sub>	
13	284.0	120.0	30.0	50.0	16.0	12.0	10.0	6.0	170.0	-	4, (NH <sub>4</sub> ) <sub>2</sub> Fe(SO <sub>4</sub> ) <sub>2</sub>	
14	215.0	160.0	40.0	66.7	30.0	12.0	10.0	6.0	170.0	-	4, (NH <sub>4</sub> ) <sub>2</sub> Fe(SO <sub>4</sub> ) <sub>2</sub>	
15	250.0	160.0	40.0	66.7	-	12.0	10.0	6.0	170.0	-	2 and 4	
16	268.0	144.0	36.0	60.0	-	12.0	10.0	6.0	170.0	-	2	
17	268.0	160.0	40.0	66.7	12.7	12.0	10.0	6.0	170.0	-	2	
18	243.7	176.0	24.0	66.7	12.7	12.0	10.0	6.0	170.0	-	1	
19	243.7	190.0	10.0	66.7	12.7	12.0	10.0	6.0	170.0	-	1	
20	243.7	184.0	16.0	66.7	12.7	12.0	10.0	6.0	170.0	-	1	
21	243.7	200.0	-	66.7	12.7	12.0	10.0	6.0	170.0	-	1	
22	241.4	200.0	-	66.7	-	12.0	10.0	6.0	170.0	-	1	

Example #	Amount of Components (Parts by Weight)										Polymerization Method #
	a	b	c	d	e	f	g	h	i	j	
23	150.0	200.0	-	66.7	8.0	12.0	10.0	6.1	151.7	-	3, (35 °C)
24	265.0	200.0	-	50.0	8.0	12.0	10.0	6.0	170.0	-	3, (35 °C)
25	243.7	200.0	-	66.7	12.0	15.0	12.5	7.5	163.0	-	3, (35 °C)
26	243.7	200.0	-	66.7	12.0	18.0	15.0	9.0	156.0	-	3, (35 °C)
27	313.4	150.0	-	50.0	9.0	12.0	10.0	6.0	170.0	-	3, (35 °C)
28	150.0	200.0	-	66.7	12.0	12.0	10.0	6.0	170.0	-	3, (35 °C)
29	265.0	200.0	-	50.0	8.0	12.0	10.0	6.0	170.0	-	3, (35 °C)
30	280.0	200.0	-	35.0	8.0	12.0	10.0	6.0	170.0	-	3, (35 °C)
31	243.7	200.0	-	66.7	12.0	36.0	30.0	18.0	160.0	-	3, (35 °C)
32	150.0	200.0	-	35.0	8.0	12.0	10.0	6.0	170.0	-	3, (35, 45 and 55 °C)
33	243.7	200.0	-	66.7	12.0	18.0	15.0	9.5	156.0	-	3, (45 °C),
34	150.0	160.0	40.0	45.0	12.0	12.0	10.0	6.0	170.0	-	3, (40 and 50 °C)

Example #	Amount of Components (Parts by Weight)										Polymerization Method #
	a	b	c	d	e	f	g	h	i	j	
35	317.0	37.0	86.3	24.7	109.4	30.0	15.0	-	250.0	8.0	5
36	336.1	32.7	76.5	32.8	95.1	30.0	15.0	-	250.0	8.0	5
37	312.0	-	120.0	12.0	130.0	30.0	15.0	-	250.0	8.0	5
38	376.0	92.0	23.0	23.0	61.3	30.0	15.0	-	250.0	8.0	5
39	381.8	92.0	23.0	28.8	61.3	30.0	15.0	-	250.0	8.0	5 (41 °C)
40	130.0	200.0	-	66.7	77.0	22.0	5.5	5.5	157.0	-	5 (41 °C)
41	130.0	200.0	-	50.0	77.0	20.0	5.0	5.0	160.0	-	5 (41 °C)
42	130.0	100.0	25.0	31.2	65.0	15.0	4.0	4.0	138.0	-	5 (41 °C)
43	130.0	200.0	-	33.3	77.0	22.0	5.5	5.5	160.0	-	5 (41 °C)
44	122.0	204.0	-	51.0	78.4	21.0	5.3	5.3	200.0	-	5 (41 °C)
45	130.0	200.0	-	50.0	77.0	22.0	5.5	5.5	190.0	-	5 (41 °C)

What is claimed is:

1. A polymer produced by polymerizing via water-in-oil emulsion polymerization one or more water soluble monomers with one or more polyalkoxylated monomers  
5 wherein said one or more polyalkoxylated monomers contains at least 25 alkylene oxide units and wherein said polymer demonstrates thermothickening properties.
2. A polymer produced by polymerizing via water-in-oil emulsion polymerization one or more water soluble monomers and grafting (poly)alkylene oxide groups onto  
10 one or more moieties of said polymerized water soluble monomers, wherein said (poly)alkylene oxide groups contain at least 25 alkylene oxide units and wherein said polymer demonstrates thermothickening properties.
3. A polymer which is the reaction product of one or more water soluble monomers  
15 and one or more polyalkoxylated monomers wherein said one or more polyalkoxylated monomer contains at least 25 alkylene oxide units and wherein said polymer demonstrates thermothickening properties and has a molecular weight of at least 2,000,000 daltons.
- 20 4. A polymer which is the reaction product of one or more water soluble monomers and which has grafted onto one or more of its moieties alkylene oxide groups, wherein said alkylene oxide groups contain at least 25 alkylene oxide units and wherein said polymer demonstrates thermothickening properties and has a molecular weight of at least 2,000,000 daltons.
- 25 5. A method for producing a polymer which demonstrates thermothickening properties by polymerizing via water-in-oil emulsion polymerization one or more water soluble monomers with one or more polyalkoxylated monomers wherein said one or more polyalkoxylated monomers contains at least 25 alkylene oxide units.
- 30 6. A method for producing a polymer which demonstrates thermothickening properties by polymerizing via water-in-oil emulsion polymerization one or more

water soluble monomers and grafting alkylene oxide groups onto one or more moieties of said polymerized water soluble monomers, wherein said alkylene oxide groups contain at least 25 alkylene oxide units.

- 5 7. A pharmaceutical composition, oil, lubricant, paint, coating, liquid cleanser, polish, food product, wax, cosmetic, personal care composition, electrophoresis composition, chromatography composition, binding composition, extrusion composition, molding composition, cementing composition or controlled release compositions including a polymer produced by polymerizing via water-in-oil emulsion polymerization one or  
10 more water soluble monomers with one or more polyalkoxylated monomers wherein said one or more polyalkoxylated monomers contains at least 25 alkylene oxide units and wherein said product demonstrates thermothickening properties.
- 15 8. A pharmaceutical composition, oil, lubricant, paint, coating, liquid cleanser, polish, food product, wax, cosmetic, personal care composition, electrophoresis composition, chromatography composition, binding composition, extrusion composition, molding composition, cementing composition or controlled release compositions including a polymer produced by polymerizing via water-in-oil emulsion polymerization one or  
20 more water soluble monomers and grafting alkylene oxide groups onto one or more moieties of said polymerized water soluble monomers, wherein said alkylene oxide groups contain at least 25 alkylene oxide units and wherein said polymer demonstrates thermothickening properties.
- 25 9. A thermothickening polymer composition which comprises: (a) a polymer of claim 1 demonstrating thermothickening properties and (b) a thermothickening enhancing effective amount of a nonionic surfactant.
- 30 10. A thermothickening polymer composition which comprises: (a) a polymer of claim 2 demonstrating thermothickening properties and (b) a thermothickening enhancing effective amount of a nonionic surfactant.



11. A thermothickening polymer composition which comprises: (a) a polymer of claim 3 demonstrating thermothickening properties and (b) a thermothickening enhancing effective amount of a nonionic surfactant.

- 5 12. A thermothickening polymer composition which comprises: (a) a polymer of claim 4 demonstrating thermothickening properties and (b) a thermothickening enhancing effective amount of a nonionic surfactant,

Figure 1. Salt Thickening of the Polymer from Example #10 (1%)

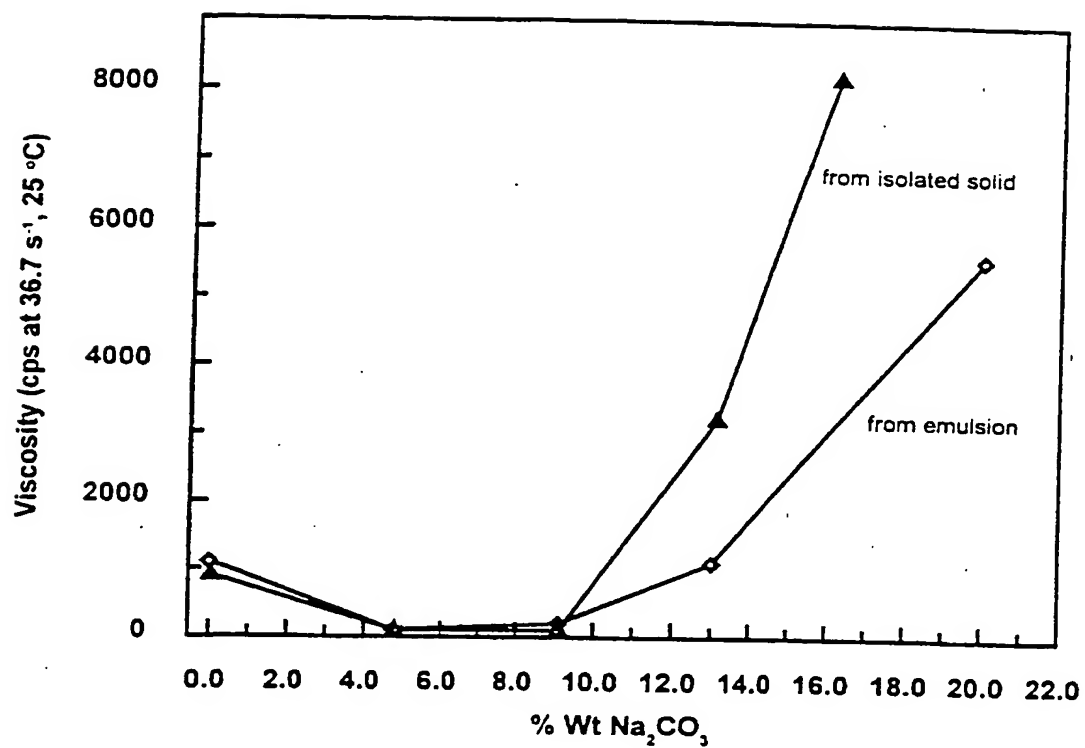


Figure 2. Thermal Thickening of the Polymer from Example #1 in Water or in 15%  $\text{Na}_2\text{CO}_3$

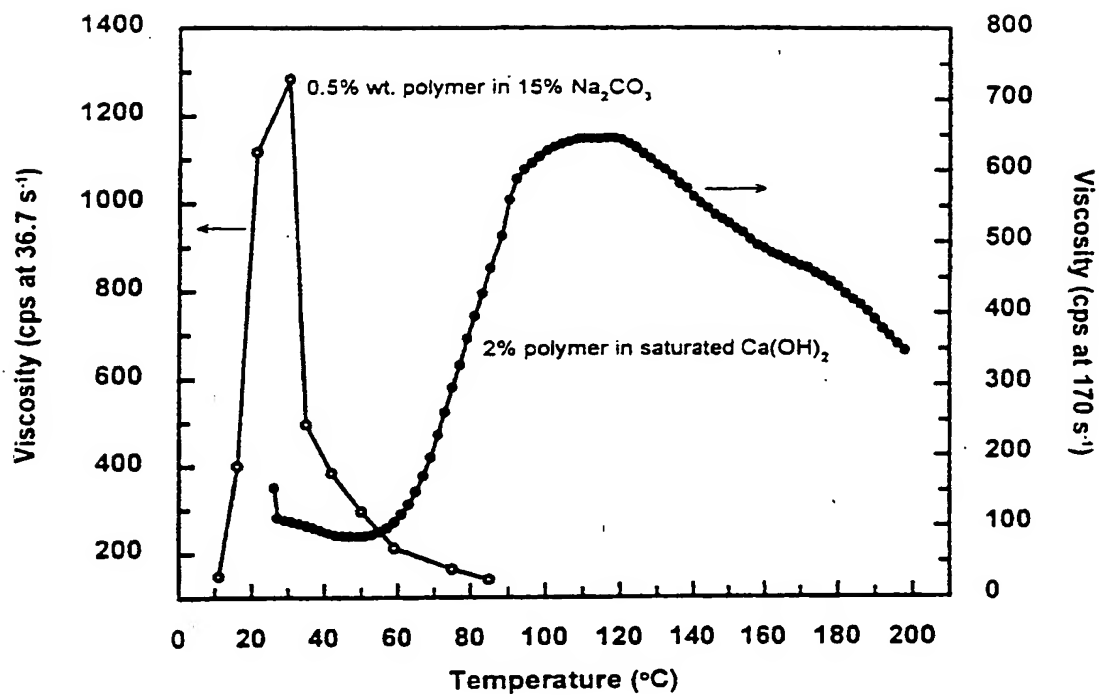


Figure 3. Thermal Thickening of the Polymer from Example #10 in Saturated  $\text{Ca}(\text{OH})_2$  or in the Presence of 15% (by Weight) Sodium Carbonate.

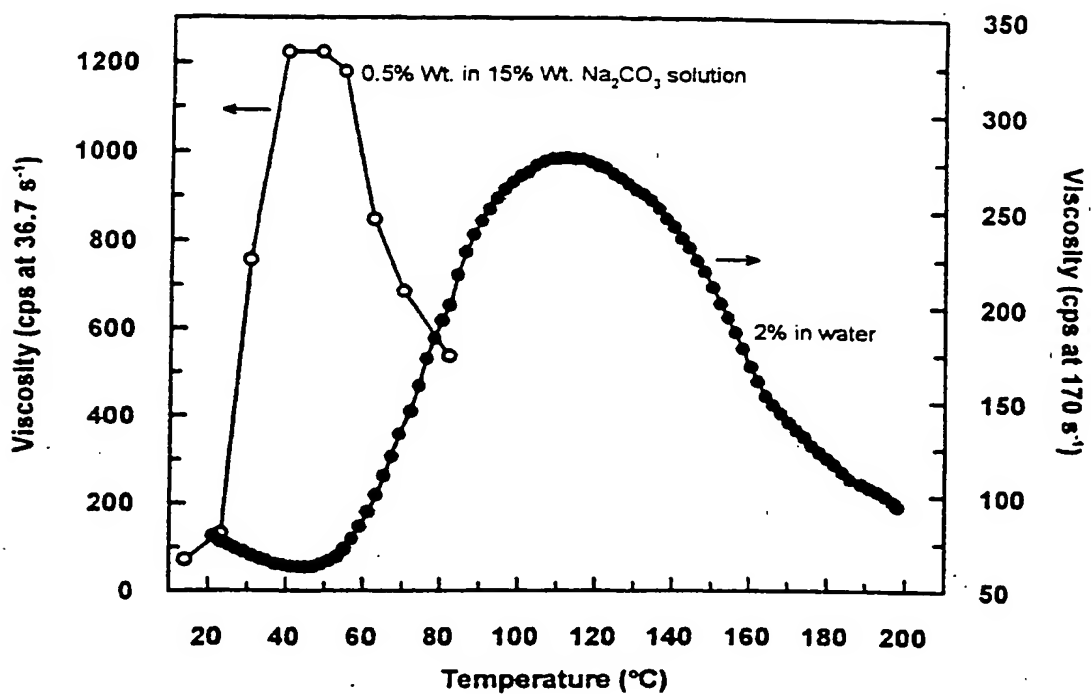


Figure 4. Thermal Thickening of the Polymer from Example #10 (1.0%) in the Presence of 15% (by Weight)  $\text{Na}_2\text{CO}_3$  ( Prepared Directly from Emulsion or from the Precipitated Solid)

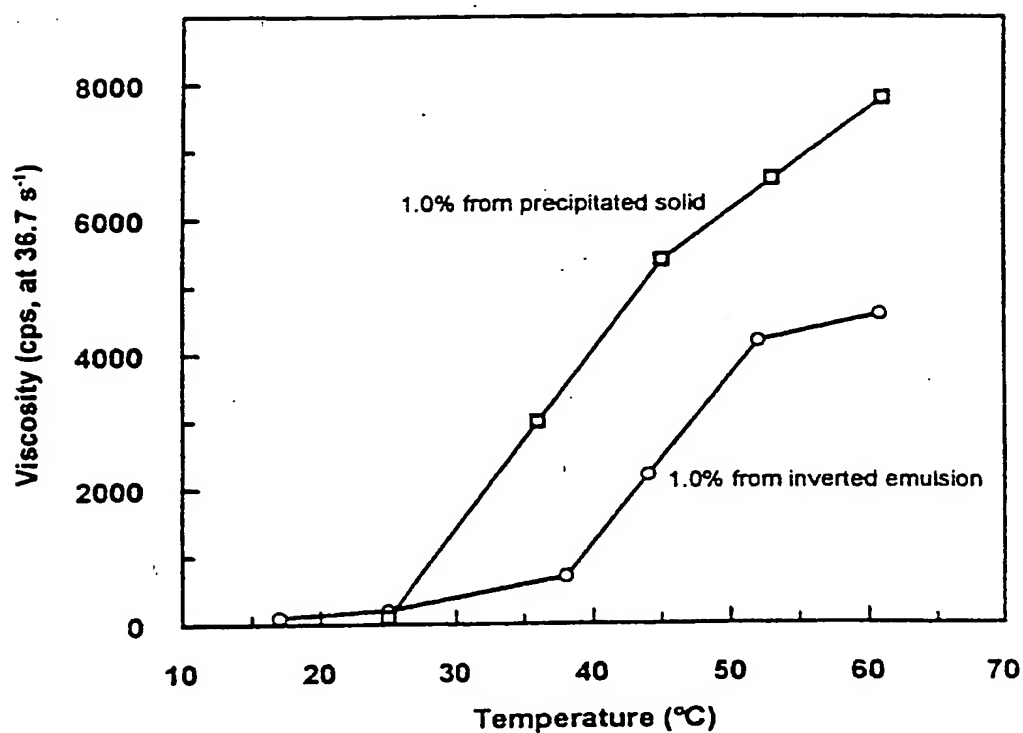


Figure 5. Shear Thickening of 1% Polymer from Example #10 (Precipitated Solid) in the Presence of 20% (by Weight) Sodium Carbonate.

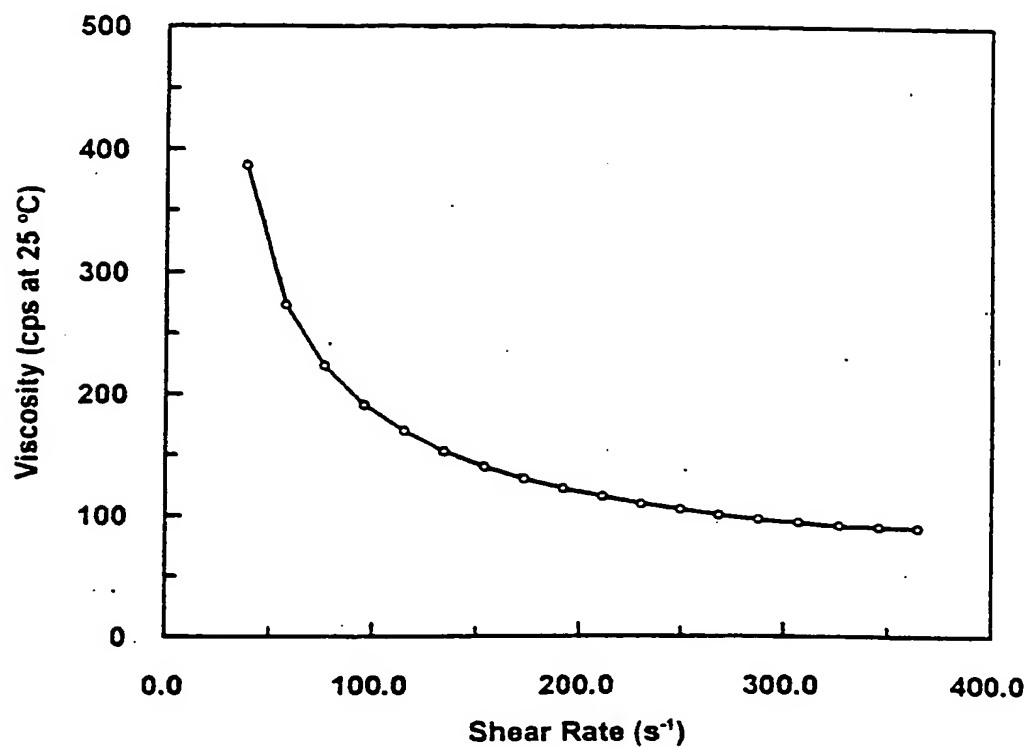


Figure 6. Thermal Thickening of Polymer from Examples #3-6 and #1 (0.5% by weight) in the Presence of 15% (by Weight)  $\text{Na}_2\text{CO}_3$  ( Prepared from the Precipitated Solid with  $\text{NaOH}$ )

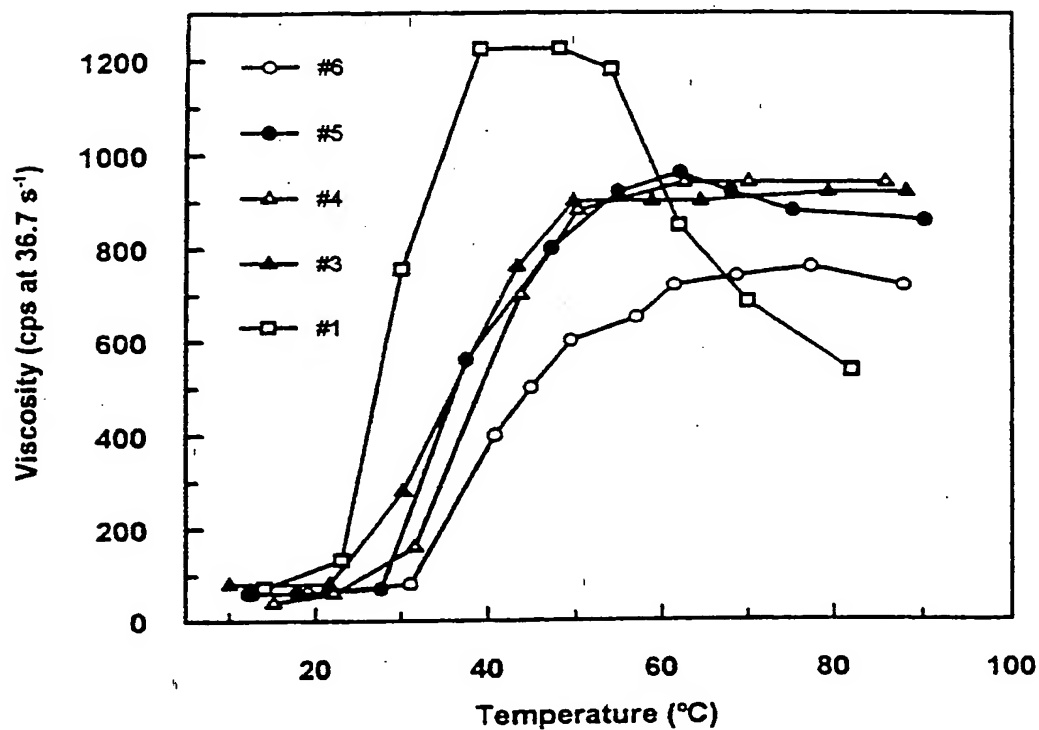
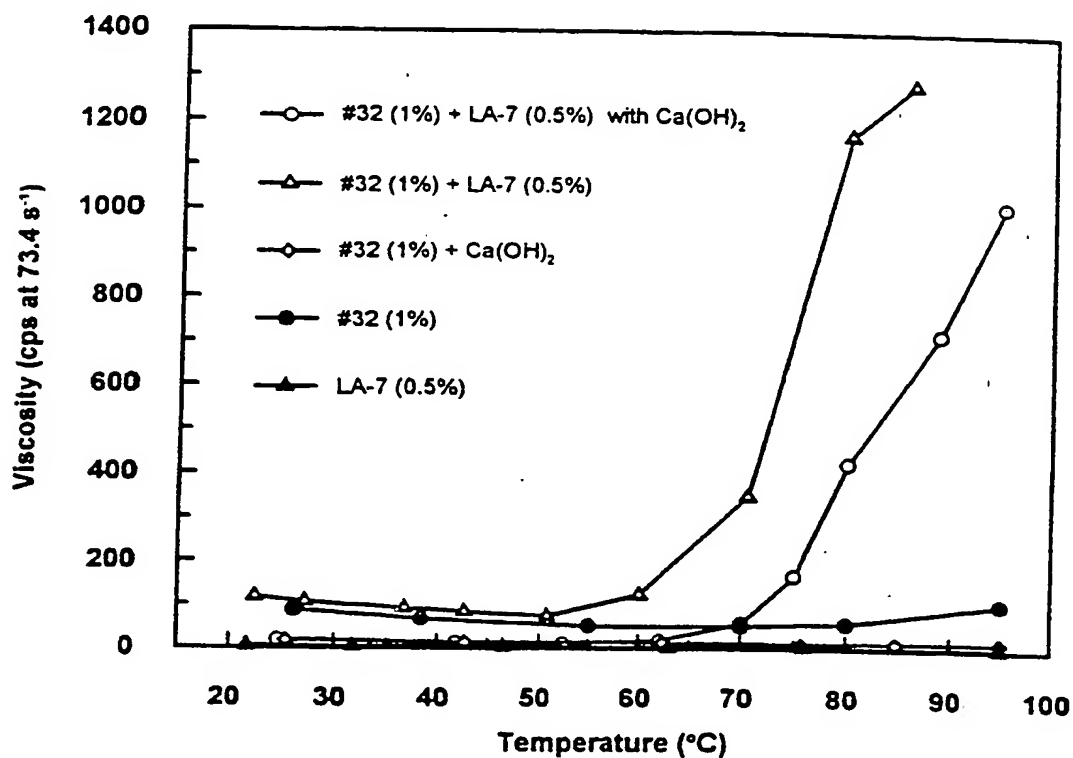


Figure 7. The Enhancement of Thermal Thickening of Polymer from # 32 in the Presence of Rhodasurf LA-7





# INTERNATIONAL SEARCH REPORT

Int. l. Application No  
PCT/US 99/29177

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 7 C08F2/32 C08F290/06 C08G81/02

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 7 C08F C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 98 51694 A (PURDUE RESEARCH FOUNDATION) 19 November 1998 (1998-11-19) page 6, line 7-11 ---	1,3,5,7
X	HOURET D ET AL: "Synthesis of thermoassociative copolymers" POLYMER,GB,ELSEVIER SCIENCE PUBLISHERS B.V, vol. 38, no. 10, 1 May 1997 (1997-05-01), pages 2535-2547, XP004059755 ISSN: 0032-3861 the whole document ---	1,2
X	US 4 892 916 A (FARRAR DAVID ET AL) 9 January 1990 (1990-01-09) column 5, line 47-57; claim 1 column 8, line 15-58 ---	1
	-/--	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### \* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date, and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "3" document member of the same patent family

Date of the actual completion of the international search

28 April 2000

Date of mailing of the international search report

11/05/2000

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040. Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Meulemans, R

# INTERNATIONAL SEARCH REPORT

Int. Application No  
PCT/US 99/29177

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 792 343 A (FARRAR DAVID ET AL) 20 December 1988 (1988-12-20) claim 1 ---	1
X	US 4 873 086 A (GOOD WILLIAM R ET AL) 10 October 1989 (1989-10-10) claim 1 ---	1
A	GB 879 950 A (UNION CARBIDE CORPORATION) 11 October 1961 (1961-10-11) page 1, line 27 -page 2, line 113 ---	2
A	WO 98 06438 A (GEL SCIENCES INC) 19 February 1998 (1998-02-19) the whole document ---	1-12
A	US 5 451 641 A (EISENHART ERIC K ET AL) 19 September 1995 (1995-09-19) column 3, line 1-44 -----	1

Form PCT/ISA/210 (continuation of second sheet) (July 1992)

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 99/29177

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9851694 A	19-11-1998	US 6018033 A	25-01-2000
		AU 7478498 A	08-12-1998
US 4892916 A	09-01-1990	AU 4621785 A	20-02-1986
		CA 1241492 A	30-08-1988
		CA 1273449 A	28-08-1990
		CA 1241149 A	23-08-1988
		DE 3583559 D	29-08-1991
		DE 3583560 D	29-08-1991
		DE 3584551 A	05-12-1991
		EP 0172723 A	26-02-1986
		EP 0172724 A	26-02-1986
		EP 0172025 A	19-02-1986
		JP 61082812 A	26-04-1986
		JP 61069803 A	10-04-1986
		JP 61081414 A	25-04-1986
		US 4940763 A	10-07-1990
		US 4980434 A	25-12-1990
		US 4677152 A	30-06-1987
		US 4702844 A	27-10-1987
		ZA 8506201 A	29-10-1986
		AT 53605 T	15-06-1990
		AT 60871 T	15-02-1991
		AU 612965 B	25-07-1991
		AU 6089786 A	19-02-1987
		BR 8603812 A	17-03-1987
		CA 1318689 A	01-06-1993
		CA 1309546 A	27-10-1992
		CA 1286445 A	16-07-1991
		CA 1264280 A	09-01-1990
		CA 1295778 A	11-02-1992
		EP 0213799 A	11-03-1987
		EP 0213800 A	11-03-1987
		EP 0215565 A	25-03-1987
		EP 0214760 A	18-03-1987
		EP 0216479 A	01-04-1987
		JP 2530433 B	04-09-1996
		JP 62042731 A	24-02-1987
		JP 2085247 C	23-08-1996
		JP 7112994 B	06-12-1995
		JP 62039537 A	20-02-1987
		JP 2553841 B	13-11-1996
		JP 62057408 A	13-03-1987
		JP 62039608 A	20-02-1987
		US 5210324 A	11-05-1993
		US 4792343 A	20-12-1988
		US 4741790 A	03-05-1988
		ZA 8605945 A	28-10-1987
US 4792343 A	20-12-1988	AT 53605 T	15-06-1990
		AT 60871 T	15-02-1991
		AU 4621785 A	20-02-1986
		AU 612965 B	25-07-1991
		AU 6089786 A	19-02-1987
		BR 8603812 A	17-03-1987
		CA 1241492 A	30-08-1988
		CA 1318689 A	01-06-1993
		CA 1309546 A	27-10-1992

# INTERNATIONAL SEARCH REPORT

Information on patent family members

Int. Patent Application No

PCT/US 99/29177

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4792343 A		CA 1286445 A	16-07-1991
		CA 1264280 A	09-01-1990
		CA 1295778 A	11-02-1992
		DE 3583559 D	29-08-1991
		DE 3583560 D	29-08-1991
		DE 3584551 A	05-12-1991
		EP 0172723 A	26-02-1986
		EP 0172724 A	26-02-1986
		EP 0172025 A	19-02-1986
		EP 0213799 A	11-03-1987
		EP 0213800 A	11-03-1987
		EP 0215565 A	25-03-1987
		EP 0214760 A	18-03-1987
		EP 0216479 A	01-04-1987
		JP 2530433 B	04-09-1996
		JP 62042731 A	24-02-1987
		JP 2085247 C	23-08-1996
		JP 7112994 B	06-12-1995
		JP 62039537 A	20-02-1987
		JP 2553841 B	13-11-1996
		JP 62057408 A	13-03-1987
		JP 62039608 A	20-02-1987
		US 4892916 A	09-01-1990
		US 4940763 A	10-07-1990
		US 4980434 A	25-12-1990
		US 5210324 A	11-05-1993
		US 4702844 A	27-10-1987
		US 4741790 A	03-05-1988
		ZA 8605945 A	28-10-1987
US 4873086 A	10-10-1989	NONE	
GB 879950 A		BE 571756 A	
		CH 392068 A	
		DE 1100950 B	
		FR 1204449 A	26-01-1960
		NL 111374 C	
		NL 226509 A	
WO 9806438 A	19-02-1998	EP 0920338 A	09-06-1999
US 5451641 A	19-09-1995	US 5266646 A	30-11-1993